

## **Project Report**

**Project Title: A Compact Airborne System for SO<sub>2</sub> and DMS Measurements for use on Future GTE Missions Aboard the P-3 or DC-8.**

**Grant Number: NAG-12002**

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This project involved the design and construction of a new instrument for airborne measurement of DMS and SO<sub>2</sub>. The instrument is intended for use on field missions to study the global atmospheric sulfur cycle. The ultimate scientific goal is to provide insight into the mechanisms of atmospheric transport and transformations impacting both natural and anthropogenic sulfur emissions. This report summarizes the progress made to date, and the goals for future work on the project. The PI's for this project have recently relocated from the University of Miami to the University of California, Irvine and a request has been made to transfer remaining funds to UCI. All equipment associated with this project has been transferred to UCI.

The instrument design goal was to develop an instrument roughly ¼ the size and weight of currently available airborne instrumentation used for DMS and SO<sub>2</sub> measurements. Another goal was full automation, to allow unattended operation for the duration of a P-3 or DC-8 flight. The original performance design specifications for the instrument are given below in Table 1.

**Table 1. Performance design specifications**

	Design Objectives
Detection limit	< 5 pptv, with a goal of 1 pptv
Precision	< ±5%, with a goal of ±1%.
Measurement Period	<10 minutes, with a goal of 5 minutes
Data processing	in-flight data processing
Size	~ 13 ft <sup>3</sup>
Weight	~ 100 kg
Operation	Fully automated
Power	< 2 kW

### **Accomplishments to date:**

An isotope dilution GC/MS instrument has been designed constructed and tested in the laboratory and at two ground-based sites in the field. The instrument meets all of the original design specifications. Key aspects of the design and operation are outlined below. This is followed by a discussion of current system performance and results from two recent deployments. Inlet modifications needed for airborne deployment are also discussed.

### **a) Instrument design**

The system utilizes an air inlet manifold, cryogenic pre-concentration of air samples, GC separation, MS detection and isotopically labeled internal standards. The air

is spiked prior to entering the main manifold with isotopically labeled dimethylsulfide and sulfur dioxide in nitrogen, to generate a concentration of a few hundred pptv of the labeled compounds. Two separate sample streams, for DMS and SO<sub>2</sub>, are drawn from the main manifold. The SO<sub>2</sub> stream is dried using a combination of Nafion driers and a dry-ice/ethanol trap. The DMS sample stream is dried using a Nafion dryer and is scrubbed of oxidants by passing the stream through a canister of cotton.

Sulfur gas detection is carried out using a Hewlett Packard model 5973 mass selective detector (MSD). The basic difference between the MSD and conventional quadrupoles is the use of small hyperbolic, gold-metallized quartz quadrupoles (0.35" diameter of the inscribed circle). This has the benefit of lowering the voltage and power requirements for generating the radio frequency field needed for quadrupole tuning, compared to instruments with cylindrical machined poles. As a result, this instrument is considerably smaller and lighter.

Teflon cryotrap are mounted inside the neck of a 10 L pressurizable liquid argon dewar. The liquid argon level is pneumatically raised and lowered to immerse and expose the traps. The traps are resistance heated while exposed to desorb the analyte gases. Traps are cooled to -190°C in less than 30 seconds and reach 100°C in under 1 minute. The 10 L dewar operates for over 24 hours running a sample every 10 minutes on a single fill.

The master controller for the system is a single-board computer, running Win98. The PC is programmed to carry out control functions for valve switching, cryotrap operation, and data logging of flow rates and temperatures to monitor system performance. Data acquisition and control of the mass spectrometer is accomplished by multi-tasking with the Windows-based commercial software designed for the HP MSD (G1701AA and HPIB interface). Communication between the control program and the HP software is carried out via the Dynamic Data Exchange protocol.

## **b) Instrument performance**

Based on the mass spectrometer (HP 5973) signal to noise, we estimate the detection limits for both SO<sub>2</sub> and DMS to be better than 1.5 femtomoles. This implies that, with no loss of SO<sub>2</sub> or DMS in the system, the instrument is capable of detecting less than 5 pptv in a 1 L sample. However, the effective detection limit depends on the loss of analyte in the system under field conditions, the isotope ratios in the standards and the concentration of the standard in the manifold. The recovery of DMS through the system is generally quantitative and the recovery of SO<sub>2</sub> is typically better than 70%. In Figure 1 we show chromatograms of ions 66, 64, 68, and 62 for a typical ambient marine air sample collected outside our laboratory on Virginia Key, FL. The isotope spikes are approximately 400 pptv and 260 pptv for DMS and SO<sub>2</sub> respectively, and the ambient SO<sub>2</sub> and DMS levels are about 150 pptv and 50 pptv, respectively. The DMS is analyzed on a 3ft Carboxen B column at a flow rate of 3 mL/min and 85°C. The SO<sub>2</sub> is analyzed on a 12 ft 12% polyphenyl ether/1% H<sub>3</sub>PO<sub>4</sub> on 40/60 Chromosorb T column at a flow rate of 3 mL/min at 60°C. We estimate the lower limit of detection to be 5 pptv of DMS and SO<sub>2</sub> and the accuracy and precision of measurements to be better than 20% and 5% for both DMS and SO<sub>2</sub> respectively. In this configuration, both species elute in less than

8 minutes with the overall sample turn around time being 10 minutes. This can be reduced to 5 minutes relatively easily.

The instrument's response to DMS has been compared to a GC/FPD instrument in the field. The response is plotted relative to the GC/FID instrument response in Figure 2. Because of differences in resolution the response of the instrument is an average of 3 measurements. There is a linear correlation between instruments ( $R^2 = 0.91$ ) and the GC/FPD instrument has a response of 0.88 relative to the isotope dilution GC/MS instrument. Given the uncertainties associated with each instrument and the different measurement time scales, overall the instruments agreed well and there appears to be no significant systematic differences between instruments.

### **c) Recent deployments**

Over the last year the instrument has been deployed in two ground-based field experiments. In February-March 2000 the instrument was used to measure DMS and  $\text{SO}_2$  at Baring head, New Zealand and in April 2000 the instrument was used to measure DMS and  $\text{SO}_2$  during the SEAS intensive at Bellows Air force base in Hawaii. The goal of these deployments was two fold. First, we hoped to test the instrument in the field measuring DMS and  $\text{SO}_2$  over as wide a dynamic range of atmospheric levels as possible. This would include intercomparisons with other instruments where possible. Second, we hoped to determine to what extent  $\text{SO}_2$  yields from DMS oxidation vary with latitude. This would involve measuring DMS and  $\text{SO}_2$  over a number of diurnal cycles in clean conditions at both sites and with the aid of a photochemical box model determining  $\text{SO}_2$  yields and total  $\text{SO}_2$  sinks. Key results from these deployments include:

- The instrument performed up to specification at both sites successfully measuring DMS and  $\text{SO}_2$  over most of the atmospheric range [see figure 3].
- Anti-correlated diurnal cycles of  $\text{SO}_2$  and DMS consistent with  $\text{SO}_2$  production via DMS oxidation were observed in clean conditions at both sites [see figure 4].
- Yields of  $\text{SO}_2$  at Baring Head were 30-70% and yields of  $\text{SO}_2$  in Hawaii were 80-100% suggesting a decrease in yield with latitude.
- Total  $\text{SO}_2$  sinks were  $1.3\text{-}2.4 \times 10^4 \text{ mol cm}^{-3} \text{ s}^{-1}$  at Baring head and were  $0.5\text{-}0.7 \times 10^4$  in Hawaii. Corresponding  $\text{SO}_2$  lifetimes were  $\sim 0.5$  days at Baring Head and  $\sim 1$  day in Hawaii.

### **Future work:**

There are a number of minor modifications that we would like to make to the instrument over the next year to make it flight ready. These include replacing the existing magnetic bearing turbo pump with a ceramic bearing pump (for ruggedness) and developing and testing a constant flow inlet. The constant flow in the main manifold would provide a constant dilution ratio of the isotope dilution spike to the ambient air, allowing us to maintain optimal precision during flight. There are also several improvements to the chromatography that we would like to investigate in order to improve sample throughput and sensitivity.

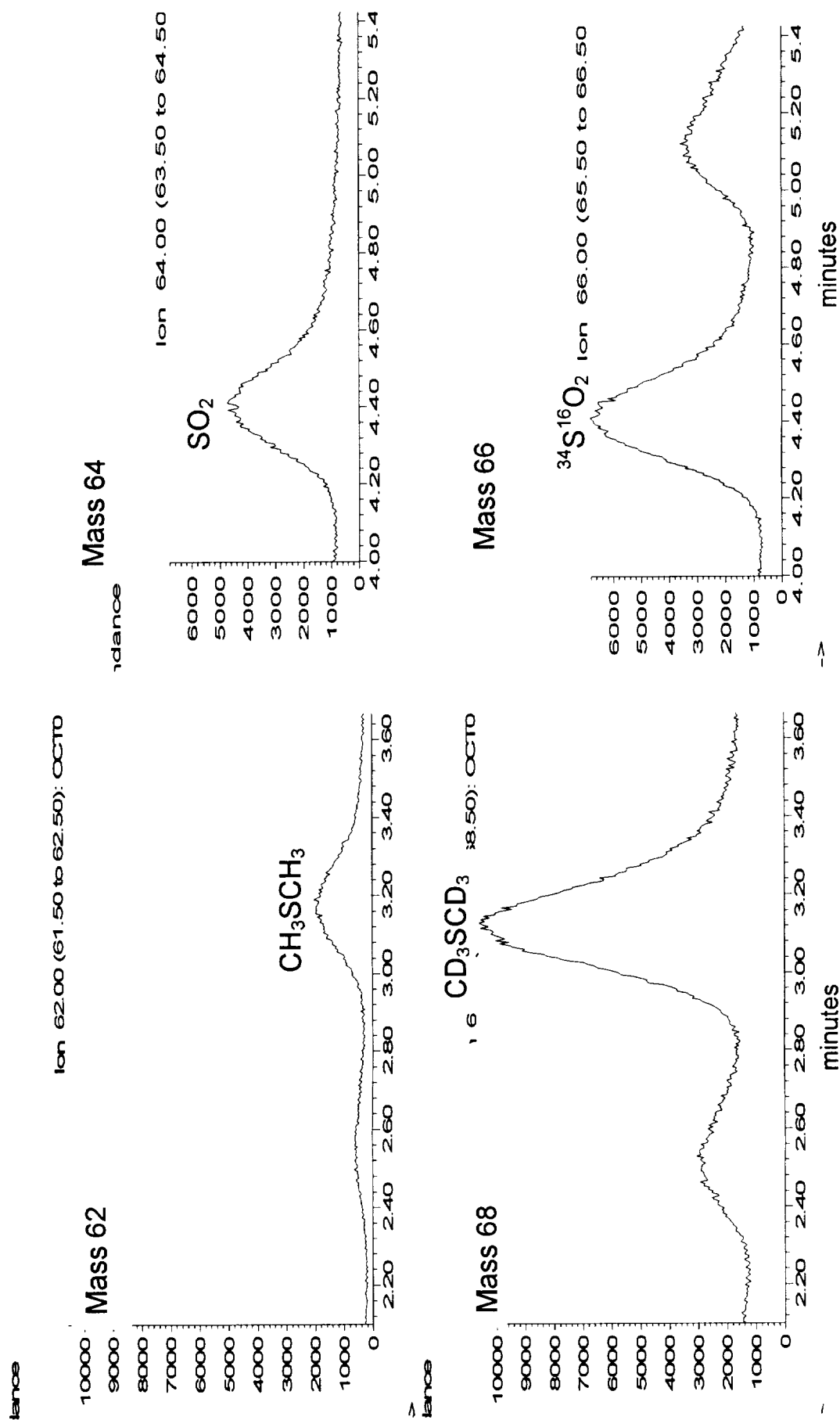
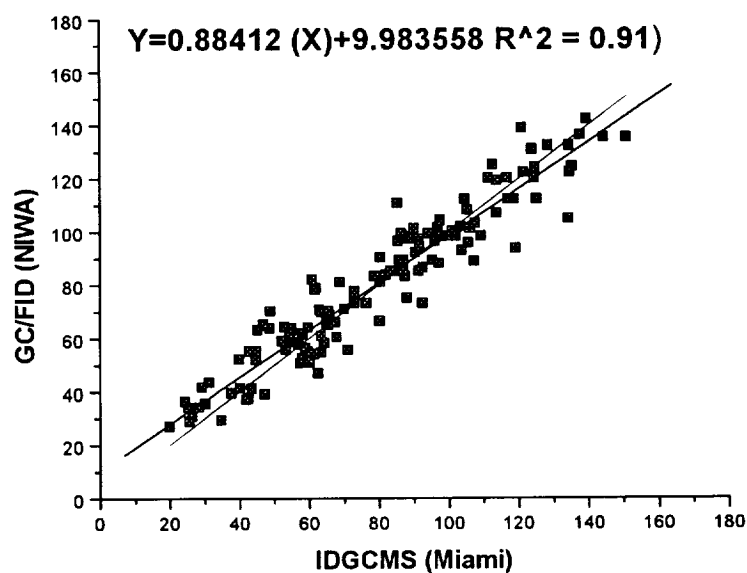
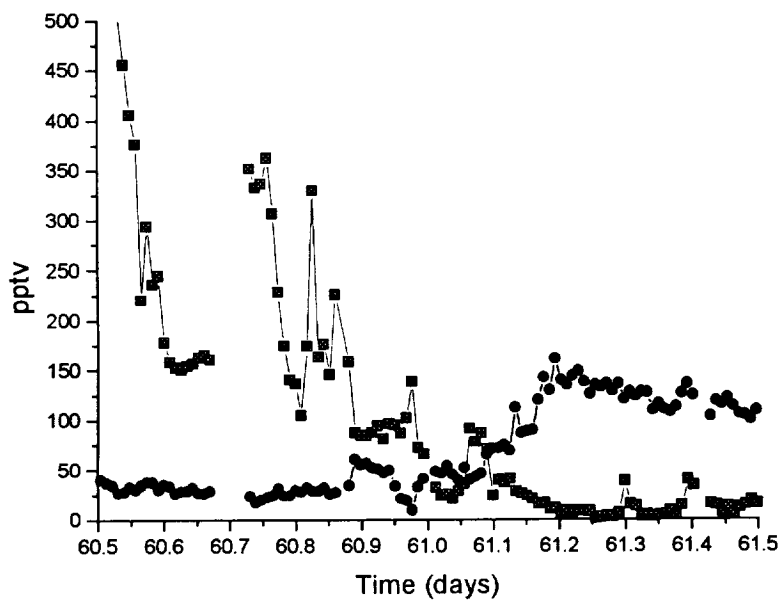


Figure 1. Instrument output from a 600 cc Miami air sample. The left panel shows the response from approximately 50 pptv DMS, with the parent ion of the ambient DMS ( $m/e=62$ ) in the upper plot and the 400 pptv isotope spike ( $\text{CD}_3\text{SCD}_3$ ;  $m/e=68$ ) in the lower plot. The right panel shows the response from approximately 60 pptv  $\text{SO}_2$ , with the parent ion of the ambient  $\text{SO}_2$  in the upper plot and the 260 pptv isotope spike ( $^{34}\text{S}^{16}\text{O}_2$ ) in the lower plot.



**Figure 2.** Instrument response for DMS relative to the response of a GC/FID instrument for measurements at Baring Head, New Zealand.



**Figure 3.** DMS and SO<sub>2</sub> levels measured at Baring Head New Zealand during a transition from relatively polluted northerly winds to clean southerly winds.

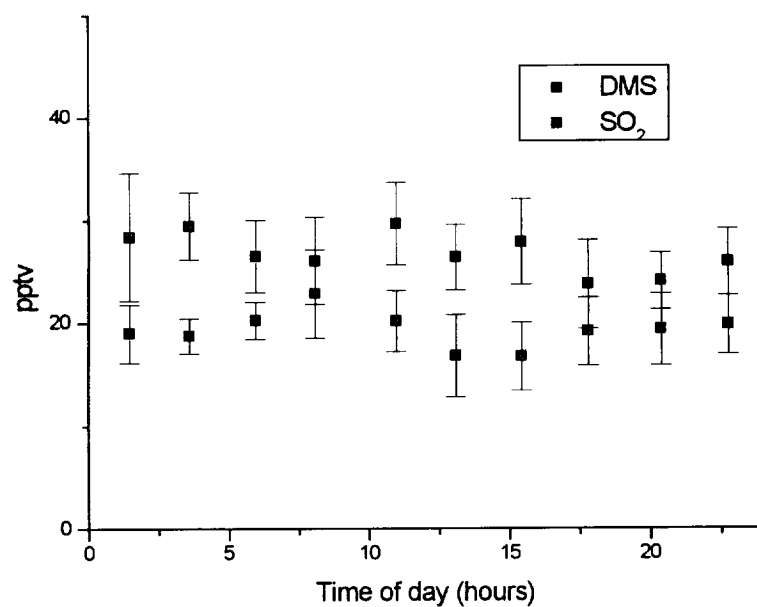


Figure 4. DMS and SO<sub>2</sub> measurements at Bellows Air Force Base Hawaii. The data has been averaged hourly over a single day. Error bars are 1 standard deviation of the mean.